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GEOCHEMISTRY OF DISPERSED NICKEL AND COBALT IN THE BIOSPHERE

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/The results of the work described here, and the methods used in work of this type, in general, are being applied in prospecting for cobalt, nickel, manganese, and other metals.

Only those figures and tables mentioned in the following text have been reproduced, and they are appended./

A method was developed for the polarographic determination of small quantities of nickel, cobalt, copper, zinc, and cadmium on the basis of their isolation by means of rubeanic acid /dithio-oxamide/ in the presence of citric acid. The method permits the determination, with an accuracy to 2-3%, of very small quantities of these elements in rocks, soils, indigenous waters, organisms, etc. (less than $1.0 \cdot 10^{-6}$%); and, moreover, makes it possible to broaden the field of polarographic research to cover other chemical elements which are no less important in respect to geochemistry, such as antimony, bismuth, lead, indium, etc.

On the basis of numerous polarographic determinations of nickel and cobalt, it was determined that they appear as dispersed chemical elements in the biosphere. For example, the average content of nickel in soils is equal to $4.0 \cdot 10^{-3}$%, and of cobalt $1.0 \cdot 10^{-3}$%; in indigenous surface water, nickel $3.4 \cdot 10^{-7}$%, cobalt $2.1 \cdot 10^{-7}$%; and in the living matter of organisms, nickel $5.2 \cdot 10^{-5}$%, cobalt $1.7 \cdot 10^{-5}$%.

The quantitative data which we obtained on the distribution of nickel and cobalt in certain rocks, soils, indigenous waters, and organisms, as well as the data given in literature in this connection, permitted us to establish the extremely interesting fact that the ratio between the content of cobalt and nickel in the biosphere is occasionally disturbed. Thus, the known ratio between the content of

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cobalt and nickel in volcanic rocks, which is equal, according to the data of Vogt, F. Clarke and Washington, V. I. Vernadskiy, A. E. Fersman, and others, to 1:10 (20), is upset in soils, indigenous surface waters, organisms, and others (see Figure 2). For example, the ratio between the content of cobalt and nickel in soils is 1:4, in the living matter of organisms 1:3 (5), in indigenous surface waters 1:1.6, etc.

Besides, a direct relationship is often observed between the content of iron and nickel, on the one hand, and manganese and cobalt, on the other, both in organisms and in other bodies of the biosphere (see Table 31).

A study of the migration of nickel and cobalt according to the soil levels has permitted the establishment of the fact that the content of cobalt and copper increases relative to the content of nickel in low soil levels; and, conversely, that there is a high content of nickel in high humus horizons of soils. The relative concentration of nickel in high soil horizons (see Table 7) leads, in the final analysis, to its more vigorous erosion from soils into rivers and the sea. This probably explains the change in the ratio between the cobalt and nickel content in soils, from the known content for volcanic rocks, in the direction of comparative enrichment of cobalt. It was also established that nickel in soils is concentrated in the iron hardpans and "ortzands," and cobalt in the corresponding ferromanganese soil occurrences, which is probably connected with the particular geochemical activity of microorganisms in each individual case.

The process of the formation of hardpans and "ortzands" in podsol soils is widely distributed in the northern regions of the Soviet Union.

The ratio between the cobalt and nickel content in river waters does not correspond to their ratio in soils. If the ratio of cobalt to nickel in soils is 1:4, in many rivers it is 1:2. Moreover, in sea and river silts the ratio of cobalt to nickel also sharply differs from their correlation in indigenous surface waters and on the average is equal to 1:4.

Investigation of the zonal soils of the USSR which are not connected with deposits of heavy metals showed the greatest content of nickel and cobalt to be in black-earth soils (nickel $7.7 \cdot 10^{-3}$% and cobalt $1.3 \cdot 10^{-3}$%) and the least quantity of them to be in grey, semidesert soils (nickel $1.0 \cdot 10^{-3}$%, cobalt $3.4 \cdot 10^{-4}$%) and in podsol soils. Such unequal distribution of nickel and cobalt in soils indicates, on the one hand, the known accumulation of heavy metals in black earth soils; and, on the other hand, of their noticeable dispersion in conditions of podsol formation and in desert and semidesert conditions.

Nickel and cobalt, like certain other heavy metals (iron, manganese, copper, etc.) in known optimum quantities are necessary elements for the activity of plants and animals. An insufficient content of cobalt and nickel in certain desert soils (Australian and others) produces an unusual endemic disease in cattle and, probably, influences the character of the vegetation in these regions. An excessive content of nickel and cobalt in soils (Central and Southern Urals and elsewhere) favors certain plants (herbaceous) and probably acts destructively on others (deciduous trees). This permits one to consider the possibility of special adaptation and cultivation of certain plants in similar soils.

The increase of nickel and cobalt content in soils and plants over the nickel deposits of the Southern Urals a hundred times over their usual contents in soils permits the mapping, by means of soil and plant analysis, of the limits of the extent of nickel and cobalt deposits as well as the carrying out of prospecting for new deposits of nickel and cobalt. This method would be convenient to apply to the conditions of the Central and Southern Urals, the lower reaches of the Ural Mountains in the Kazakh Republic, and elsewhere.

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The paths of migration of nickel and cobalt in the biosphere, as of practically all heavy metals, coincide in many respects. They start out from their places of origin as volcanic rocks, thermal springs, primary deposits, and such, and end up in the seas and oceans. Many thousand tons of these elements enter marine sediments, from which under favorable conditions they pass again into solution, or are buried under terrigenous or other marine sediment and are removed from the geochemical migration for a long time. This whole path of the migration of nickel and cobalt in the biosphere may be presented as a flow chart (see Figure 3).

The data of the present work emphasize the fact that the life processes are necessary for the migration of nickel and cobalt in the earth's crust. These processes change the correlation between these elements and lead to the relative concentration of cobalt in soils, indigenous waters, silts, organisms, etc., testifying to the greater mobility and dispersion of cobalt in comparison with nickel in the conditions of the biosphere.

In conclusion, I consider it my duty to express my thanks to Academician V. I. Vernadskiy and A. P. Vinogradov, Corresponding Member, Academy of Sciences USSR, for a series of useful suggestions for carrying out the present work.

/Appended figures and tables follow:/

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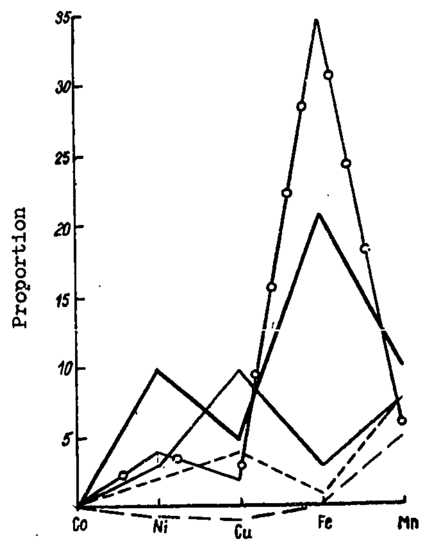

Figure 2. Proportion of Clarkes /number expressing in percent the relative occurrence of an element/ of Co, Ni, Cu, Fe, and Mn, in the Earth's Crust, Soil of the Hydrosphere, Living Matter, etc.

——— Clarkes of earth's crust

o——o Soils

- - - Hydrosphere

——— Living matter

— — Asbolite and microorganisms

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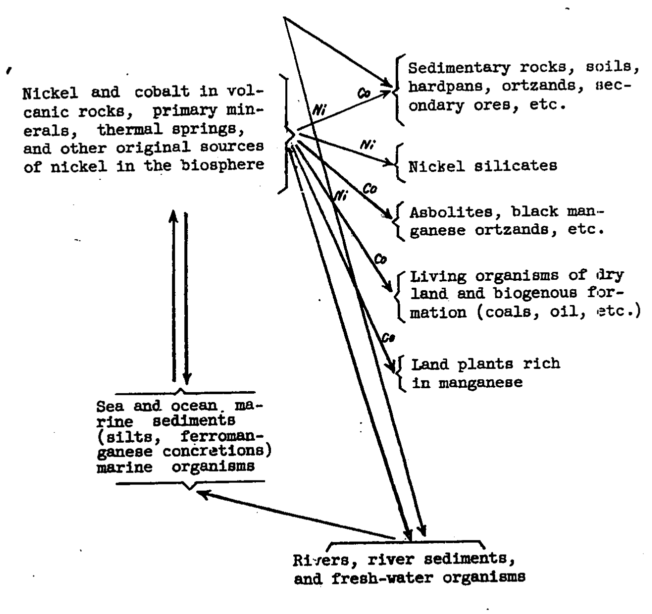

Figure 3. Migration of Nickel and Cobalt in the Biosphere

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Table 7. Percent of Content of Cu, Ni, and Co in Clayey (ordinary) Black Earth:

Level	Depth From Which Sample Was Taken Cm	Metals Found in Dry Soil Cu	Ni	Co
A_1	0-5	$1.7 \cdot 10^{-3}$	$3.9 \cdot 10^{-3}$	$6.7 \cdot 10^{-4}$
A_2	24-32	$1.2 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	$5.6 \cdot 10^{-4}$
B	80-88	$1.9 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$	$7.5 \cdot 10^{-4}$
C	128-144	$1.6 \cdot 10^{-3}$	$4.8 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$

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Table 31. Weight of Co, Ni, Cu, Fe, and Mn

	Content of metals, %					Ratio	
	Co	Ni	Cu	Fe	Mn	Co:Ni:Cu:Fe:Mn	Author
Average Clarkes of earth's crust	$2.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$	4.2	$1.0 \cdot 10^{-1}$	1:10:5:2100:50	From Clarke and Washington, A. Ye. Fersman, and our data
Basic rocks	$8.0 \cdot 10^{-3}$	$1.6 \cdot 10^{-1}$	$1.6 \cdot 10^{-2}$	13.5	$1.8 \cdot 10^{-1}$	1:20:2:1625:22	From Clarke and Washington, A. Ye. Fersman and our data
Neutral rocks	$6.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-2}$	$2.4 \cdot 10^{-2}$	10.4	$1.5 \cdot 10^{-1}$	1:5(10):4:1733:25	From Clarke and Washington, A. Ye. Fersman, and our data
Acid rocks	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-3}$	5.01	$1.0 \cdot 10^{-1}$	1:1(2):2:5100:100	From Clarke and Washington, A. Ye. Fersman, and our data
High-temperature sulfides	$2.1 \cdot 10^{-1}$	3.14	1.09	53.90	$8.0 \cdot 10^{-2}$	1:15:5(40):257:04	From I. and V. Noddak
Sedimentary rocks	$2.0 \cdot 10^{-3}$	$6.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	4.35	$4.0 \cdot 10^{-2}$	1:3:2:2170:20	From Clarke and our data
Soils	$1.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	3.5	$3.0 \cdot 10^{-2}$	1:4:2:3500:30	Our data
Hydrosphere	$2.1 \cdot 10^{-7}$	$3.4 \cdot 10^{-7}$	$4.1 \cdot 10^{-6}$	$5.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-7}$	1:1.6:20:24:2	Our data
Living matter	$1.7 \cdot 10^{-5}$	$5.2 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	$5.1 \cdot 10^{-3}$	$7.5 \cdot 10^{-4}$	1:3:10:300:40	Our data
Terrigenous marine silt	$1.1 \cdot 10^{-3}$	$3.6 \cdot 10^{-3}$	$6.8 \cdot 10^{-4}$	$4.6 \cdot 10^{-1}$	$7.5 \cdot 10^{-3}$	1:3:0.5:420:7	From Clarke
Marine concretions	$1.7 \cdot 10^{-1}$	$7.4 \cdot 10^{-1}$	$2.9 \cdot 10^{-1}$	10.0	17.2	1:4:2:50:100	From Doelter
Iron-Ni-silicate ores	$2.0 \cdot 10^{-2}$	3.0	$2.0 \cdot 10^{-2}$	25.0	$1.0 \cdot 10^{-1}$	1:150:1:1200:5	From G. A. Gritsayenko and others
Limonites	$2.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-1}$	$1.0 \cdot 10^{-2}$	50.0	$5.0 \cdot 10^{-1}$	1:10:0.5:1250:25	From A. A. Arkhangel'skiy
Manganese ores (Virginia)	$2.0 \cdot 10^{-1}$	$1.6 \cdot 10^{-1}$	$2.0 \cdot 10^{2-}$	1.0	50.0	1:0.8:0.1:5:250	From Doelter
Asbolite	--	--	--	--	--	1:0.5:0.2:5:25	From Doelter

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